PCT/EP2003/011638 WO 2004/039913

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What is claimed is

- 1. A process for the preparation of luminescent polymeric fibres characterised in that the fibres are treated with a composition comprising
- (a) one or more luminescent lanthanide chelates containing three or four organic anionic ligands having at least one UV absorbing group and
- (b) one or more solvents.
- 2. A process according to claim 1 characterized in that component (a) is a compound of formula I

$$L_m-Ln^{3+}(Ch^-)_n$$
 (I),

wherein Ln represents a lanthanide,

Ch' is a negatively charged ligand containing at least one UV absorbing double bond, n denotes 3 or 4, m denotes a number from 0 to 4,

in case n is 3, m denotes a number from 0 to 4 and L is a neutral monodentate or polydentate nitrogen-, oxygen- or sulfur-containing ligand or, in case n is 4, m denotes 1 and L is a single-charged cation.

3. A process according to claim 1 characterized in that component (a) is a compound of formula II, III or IV

$$L_{m} = L_{n}^{3+} \begin{bmatrix} R_{1} & R_{2} & R_{3} \\ R_{1} & O & N \end{bmatrix}$$

$$L_{m} = L_{n}^{3+} [R_{1} - O]_{n}$$

$$(II),$$

$$(III),$$

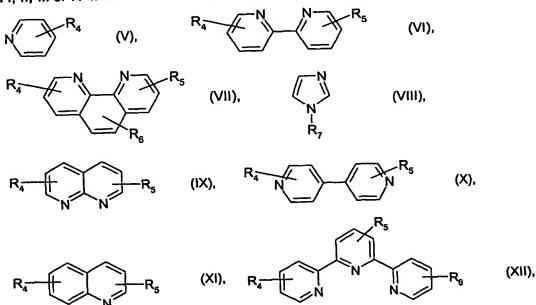
$$(IV),$$

wherein Ln represents a lanthanide, n denotes 3 or 4, m denotes a number from 0 to 4 in case n is 3, m denotes a number from 0 to 4 and L is a neutral monodentate or polydentate nitrogen-, oxygen- or sulfur-containing ligand or, in case n is 4, m denotes 1 and L is a single-charged cation,

R₂, is hydrogen or C₁-C₆alkyl, and

 R_1 and R_3 are each independently of the other hydrogen, C_1 - C_6 alkyl, CF_3 , C_5 - C_{24} aryl or C_4 - C_{24} heteroaryl.

- 4. A process according to claim 2 or 3 characterized in that component (a) is a compound of formula I, II, III or IV wherein n denotes 3 and L is a nitrogen-containing ligand.
- 5. A process according to claim 2 or 3 characterized in that component (a) is a compound of formula I, II, III or IV wherein L is a compound of formulae V to XII



or a cation of the formula $H-N^+(R_7)_3$,

wherein R_4 , R_5 and R_6 are each independently of the other hydrogen, halogen, C_1 - C_6 alkyl, C_5 - C_{24} aryl, C_6 - C_{24} aralkyl, C_1 - C_6 alkoxy, amino, dialkylamino or a cyclic amino group and R_7 is hydrogen, C_1 - C_6 alkyl, C_5 - C_{24} aryl, C_6 - C_{24} aralkyl or vinyl.

6. A process according to claim 5 characterized in that component (a) is a compound of formula II wherein L is a compound of formula V, VI, VII, VIII, IX, X, XI or XII wherein R_4 , R_5 and R_6 are hydrogen, methyl, amino, pyrrolidino or dimethylamino or L is a cation of the formula $H-N^*(R_7)_3$ wherein R_7 is C_1-C_6 alkyl.

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- 7. A process according to claim 2 or 3 characterized in that component (a) is a compound of formula I, II, III or IV wherein Ln is Eu, Tb, Dy, Sm or Nd.
- 8. A process according to claim 3 characterized in that component (a) is a compound of formula II or III wherein R₁ and R₃ are methyl, t-butyl, n-pentyl or phenyl.
- 9. A process according to claim 3 characterized in that component (a) is a compound of formula II wherein R₂ is hydrogen.
- 10. A process according to claim 3 characterized in that component (a) is a compound of formula XIII to LII

$$(H_{3}C_{2})_{2}NH = Eu^{3+} \left(\begin{array}{c} C^{-} \\ O \end{array} \right)_{3} \qquad (XXI),$$

$$(H_{3}C_{2})_{2}NH = Tb^{3+} \left(\begin{array}{c} (H_{3}C)_{3}C \\ O \end{array} \right)_{4} \qquad (XXII),$$

$$Tb^{3+} \left(\begin{array}{c} (H_{3}C)_{2}C \\ O \end{array} \right)_{5} \qquad (XXIII),$$

$$Sm^{3+} \left(\begin{array}{c} (H_{3}C)_{3}C \\ O \end{array} \right)_{7} \qquad (XXIII),$$

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$$Tb^{3+} \left(\begin{array}{c} (H_{3}C)_{3}C \\ O \end{array} \right)_{7} \qquad (XXIII),$$

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$$Tb^{3+} \left(\begin{array}{c} (H_{3}C)_{3}C \\ O \end{array} \right)_{7} \qquad (XXIII)$$

11. A process according to claim 1 or 2 characterized in that component (b) is water, one or more water-miscible organic solvents or a mixture of water and one or more water-miscible organic solvents.

- 12. A process according to claim 11 characterized in that the water-miscible organic solvent is an aliphatic alcohol, etheralcohol, glycol, aliphatic ketone, carboxylic acid ester, carboxylic acid amide, aliphatic nitrile, aliphatic polyether or aliphatic sulfoxide.
- 13. A process according to claim 11 characterized in that the water-miscible organic solvent is selected from the group consisting of ethanol, 2-butoxyethanol, ethylene glycol, propylene glycol, acetone, 2-butanone, ethyl acetate, tetrahydrofurane (THF), dimethylformamide (DMF), dimethylacetamide (DMA), N-methylpyrrolidone (NMP), acetonitrile, polyethyleneglycol dimethyether and dimethylsulfoxide (DMSO).
- 14. A process according to claim 1 characterized in that the formulation contains 0.01 to 20.0 % by weight of component (a) and 80.0 to 99.99 % by weight of component (b), based on the total amount of components (a) + (b).
- 15. A process according to claim 1 characterized in that the formulation contains additionally (c) one or more colorants.
- 16. A process for the preparation of luminescent plastics characterized in that the plastics material is extruded in the presence of 0.01 10.0 % by weight, based on the amount of polymeric material, of a compound of formula II or III according to claim 3.
- 17. A luminescent textile fibre prepared by the process according to claim 1.
- 18. A luminescent plastic prepared by the process according to claim 16.
- 19. A process according to claim 1 wherein the polymeric fibres are paper fibres or synthetic fibres.
- 20. The use of the process according to claim 1 for the preparation of anti-counterfeit documents, cards, cheques or banknotes.